

# Mercury Cycling in Stream Ecosystems. 1. Water Column Chemistry and Transport

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We studied total mercury (THg) and methylmercury (MeHg) in eight streams, located in Oregon, Wisconsin, and Florida, that span large ranges in climate, landscape characteristics, atmospheric Hg deposition, and water chemistry. While atmospheric deposition was the source of Hg at each site, basin characteristics appeared to mediate this source by providing controls on methylation and fluvial THg and MeHg transport. Instantaneous concentrations of filtered total mercury (FTHg) and filtered methylmercury (FMeHg) exhibited strong positive correlations with both dissolved organic carbon (DOC) concentrations and streamflow for most streams, whereas mean FTHg and FMeHg concentrations were correlated with wetland density of the basins. For all streams combined, whole water concentrations (sum of filtered and particulate forms) of THg and MeHg correlated strongly with DOC and suspended sediment concentrations in the water column.

## Introduction

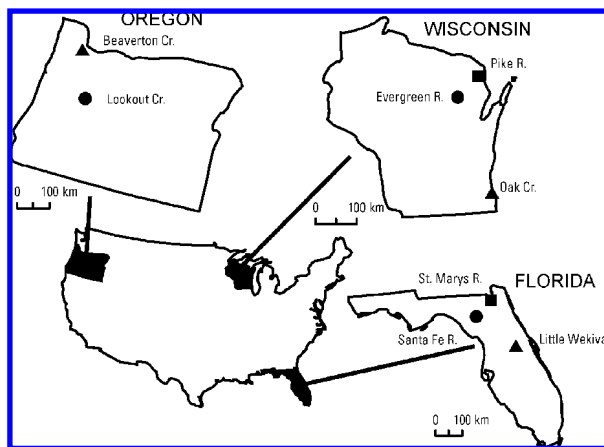
Toxicologically significant levels of methylmercury (MeHg) occur in fish in many aquatic ecosystems receiving mercury (Hg) via atmospheric deposition. Hg contamination in fish is now the most common reason for human-health-related fish-consumption advisories (1). Atmospheric deposition of Hg originating from both natural and anthropogenic sources is the predominant Hg input to most aquatic ecosystems (2). Emissions from coal-fired power plants remain the largest single source of unregulated anthropogenic Hg in the U.S. (3), and federal and state governments are currently considering options to reduce these emissions. Over the past two decades, considerable research has been conducted on Hg in lakes, reservoirs, and wetlands, leaving streams comparatively less well-studied. Streams by their nature are sensitive to atmospheric deposition due to connectivity with their watersheds. However, this responsiveness is likely dependent on the type of stream and on an abundance of wetlands, which have been associated with enhanced Hg methylation and MeHg transport (4).

To better understand environmental controls on Hg transport and bioaccumulation in stream ecosystems, we studied Hg in streamwater, streambed sediment and pore water, and selected biota in eight basins across the U.S. that receive Hg predominantly via atmospheric deposition. This study provided a unique opportunity to compare Hg biogeochemistry among stream basins that span large gradients of environmental conditions thought to influence the Hg cycle. The gradients include hydroclimatic conditions, land use and land cover, atmospheric Hg deposition, and water chemistry. In this paper, we evaluate factors influencing the stream transport of total mercury (THg) and MeHg, including particulate matter, dissolved organic carbon (DOC), and land cover in the stream basins relative to atmospheric Hg inputs to and fluvial outputs from the eight stream basins. Research on Hg biogeochemistry in streambed sediment and pore water (5) and in aquatic biota (6) from these streams is presented in companion papers.

## Experimental Design

Eight streams in Oregon, Wisconsin, and Florida were chosen for study (Figure 1, Table 1, see also ref 7). We assumed that Hg inputs to all streams were predominantly via wet and dry atmospheric deposition (2). Within each state, one urban basin and one or two nonurban basins were studied. The urban basins are comparable in terms of the extent of urban development (Table 1). The nonurban basins are primarily forested, contain varying amounts of wetlands, and are minimally affected by intensive land use. Annual precipitation was consistent among sites in both Wisconsin and Florida but varied by a factor of 2 in Oregon (Supporting Information, Table S2).

**Stream Water Chemistry.** Each stream was sampled, at a site near a stream gage, 30–47 times from May 2002 to March 2006. During October 2002 to September 2004, sampling frequency was approximately monthly, with additional sampling during high flows. Water chemistry data and methods are detailed in ref 8. Water samples for Hg were vacuum-filtered through 0.7- $\mu$ m, prebaked (550 °C) quartz-fiber filters (QFF), acidified with 6N HCl to approximately 1% HCl, and stored in the dark until an analysis of filtered total mercury (FTHg) and methylmercury (FMeHg) was conducted. QFFs were placed on dry ice and stored frozen until analyzed for particulate total mercury (PTHg) and methylmercury (PMeHg). Hg analyses were conducted at



**FIGURE 1. Stream locations. Symbols indicate urban (▲), low-wetland-density (●), and high-wetland-density (■) stream basins.**

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**TABLE 1. Study Streams, Basin Characteristics, Atmospheric Mercury and Methylmercury Inputs, and Fluvial Export of Mercury and Methylmercury**

site	primary land cover <sup>a</sup>	wetland, as percentage of basin area <sup>a</sup>	impervious surface, as percentage of basin <sup>a</sup>	stream basin area, km <sup>2</sup>	spatially averaged THg deposition, $\mu\text{g m}^{-2} \text{ year}^{-1}$			spatially averaged MeHg deposition, $\mu\text{g m}^{-2} \text{ year}^{-1}$			fluvial Hg yield (mean annual load/basin area), $\mu\text{g m}^{-2} \text{ year}^{-1}$		mean percentage of atmospheric Hg exported from basin as fluvial Hg			
					dry <sup>b</sup>	wet <sup>c</sup>	total estimate <sup>d</sup>	Hg-low estimate <sup>d</sup>	Hg-high estimate <sup>d</sup>	THg <sup>f</sup>	MeHg <sup>f</sup>	THg-low input estimate	THg-high input estimate	MeHg-wet only estimate	MeHg-high estimate	n.d. <sup>g</sup>
Lookout Creek, OR	forest	0.0	0.02	62.4	2.0	7.1	9.1	21.3	0.33	0.33	0.99	1.71	n.d. <sup>g</sup>	8	n.d. <sup>g</sup>	n.d. <sup>g</sup>
Beaverton Creek, OR	urban	0.3	39.9	95.6	3.1	4.9	8.0	14.8	0.25	0.25	0.75	3.54	44	24	8	3
Pike River, WI	forest	17.9	0.26	660.	3.2	8.8	11.9	26.3	0.18	0.18	0.54	0.90	8	3	16	5
Evergreen River, WI	forest	13.4	0.11	167.	3.1	9.7	12.8	29.0	0.17 <sup>h</sup>	0.17 <sup>h</sup>	0.52	0.87	7	3	24	8
Oak Creek, WI	urban	3.5	24.8	64.7	6.4	10.3	16.7	31.0	0.092	0.092	0.28	3.63	22	12	126	42
St. Marys River, FL	forest	35.6	0.57	1810.	3.1	15.3	18.4	45.9	0.089	0.089	0.27	4.36	24	9	64	21
Santa Fe River, FL	forest	17.9	0.81	2630.	2.7	20.3	23.0	60.9	0.060	0.060	0.18	3.68	16	6	306	102
Little Wekiva River, FL	urban	13.2	25.6	115.	4.9	19.0	23.9	57.0	0.093	0.093	0.28	1.60	7	3	130	43

<sup>a</sup> Determined from enhanced National Land Cover Data set and Land Use Land Cover data set, as described in ref 7. <sup>b</sup> Determined from geospatial coverage of model-estimated dry depositional rates, described in Supporting Information ref 4. <sup>c</sup> Wet deposition rates calculated as product of annual precipitation volume over stream basin and precipitation-volume-weighted THg (or MeHg) concentrations from nearby MDN site. See Supporting Information Table S2. <sup>d</sup> Sum of dry + wet deposition (due to rounding, displayed values for dry and wet deposition do not exactly sum to displayed value for total Hg). <sup>e</sup> Calculated as 3 times wet deposition, as explained in the text. <sup>f</sup> Calculated as mean annual THg or MeHg load for 2003–2004 (Supporting Information Table S3) divided by basin area. <sup>g</sup> Not determined; all but one MeHg concentration less than method detection limit. <sup>h</sup> MeHg not measured at this site; used precipitation-volume-weighted MeHg from nearby WI09 site to calculate MeHg deposition rate.

the U.S. Geological Survey (USGS) Mercury Research Laboratory in Middleton, Wisconsin. Concentrations of PTHg and PMeHg are expressed as the mass of Hg per volume of water that passed through the QFF during filtration. DOC, specific ultraviolet light absorbance at 254 nm (SUVA), and suspended sediment (SS) concentration were routinely measured.

**Data Analysis.** For fluvial measurements (Hg, DOC, streamflow), much of the data analysis in this paper uses base-10 logarithm-transformed data; this transformation effectively removed heteroscedasticity from the data distributions. Except for load calculations, data analyses were performed using SAS software (release 9.1.3, SAS Institute Inc., Cary, NC). Regression analysis of the data sets with no censoring [all values greater than method detection limit (>MDL)] was performed using SAS PROC REG. For data sets that include censored values (<MDL)—particularly MeHg—maximum likelihood regression analysis and calculation of the means were performed using SAS PROC LIFEREG. For maximum likelihood regressions,  $r^2$  values are “likelihood  $r^2$ ” (9). Correlations are deemed significant if  $p < 0.05$ .

Fluvial load estimates were calculated using the S-LOADEST program written for S-Plus software (David Lorenz, USGS, written communication, 2005), which is an adaptation of LOADEST (10). Through exploratory data analysis, we determined that a commonly used model (eq 1) relating log-transformed concentrations to streamflow and seasonal terms was suitable at the study sites:

$$\log[C] = \beta_0 + \beta_1 \log[Q^*] + \beta_2 \log^2[Q^*] + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) \quad (1)$$

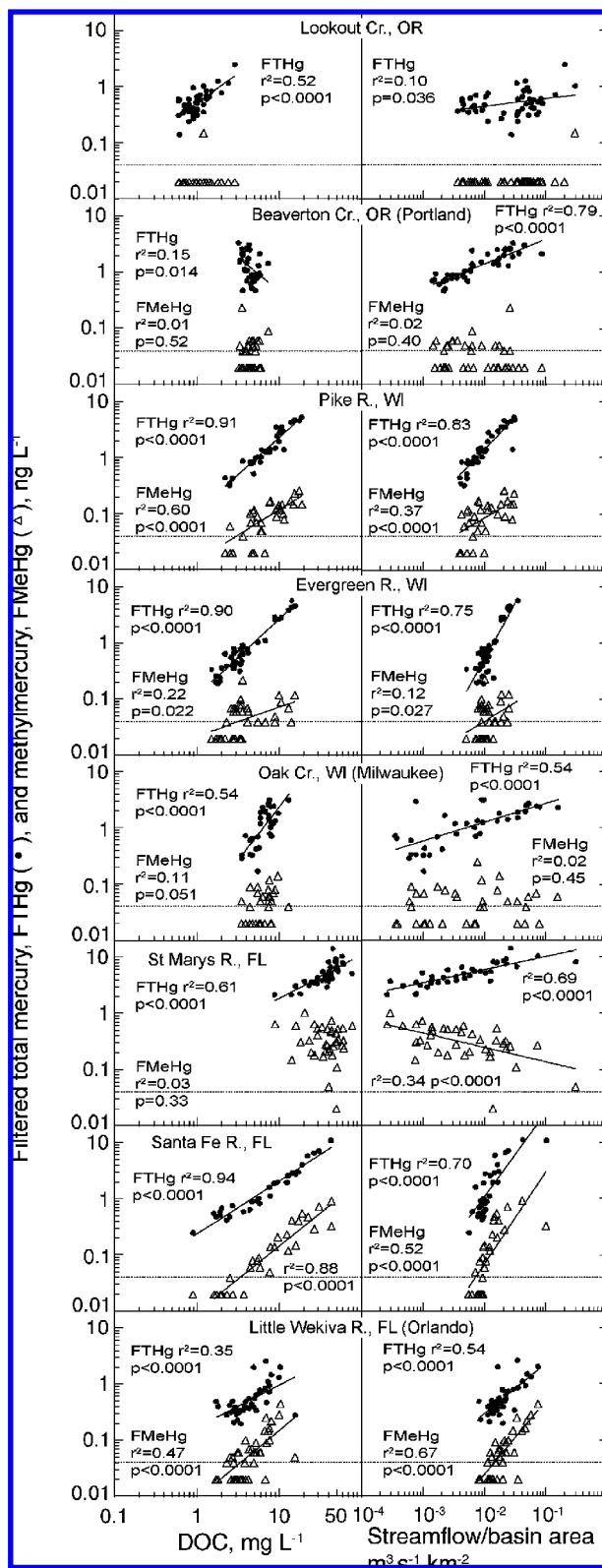
where  $C$  = measured concentration,  $Q^*$  = daily mean centered streamflow (centering described in ref 10), sine and cosine terms are included to model seasonality of the concentration-flow relationship, and  $t$  = time (in years). The  $\log^2[Q^*]$  term was significant at one to three sites, depending on constituent, and accounted for leveling off of the  $C$  versus  $Q^*$  relation at high streamflows at those sites. A similar model is used in S-LOADEST to predict fluvial Hg loads (eq 2), using the daily flow record measured at the sampling site:

$$\log[L] = \beta'_0 + \beta'_1 \log[Q^*] + \beta_2 \log^2[Q^*] + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) \quad (2)$$

where  $L$  = daily load, and  $\beta'_1 = \beta_1 + 1$  (where  $\beta_1$  is from eq 1). S-LOADEST uses the adjusted maximum likelihood estimator to account for censored data and the minimum-variance unbiased estimator to back transform regression predictions from logarithmic to arithmetic space (10). Calculated loads and upper and lower bounds of the 95% prediction intervals are provided in the Supporting Information, Table S3. Loads and yields are reported for THg (sum of FTHg and PTHg) and MeHg (sum of FMeHg and PMeHg) (Table 1).

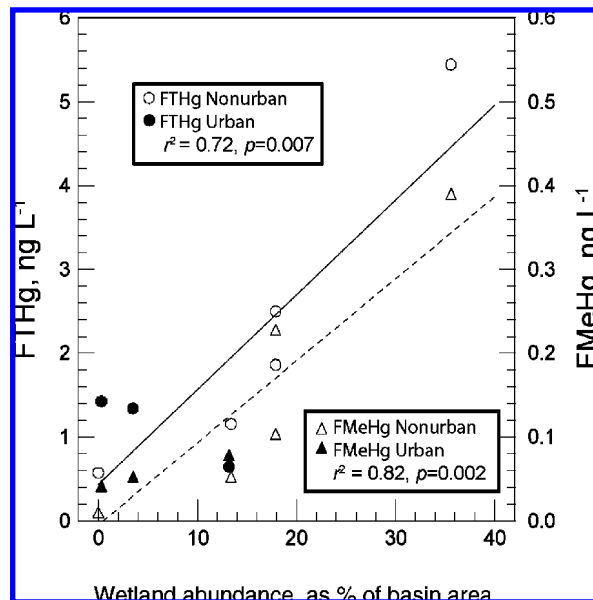
## Results and Discussion

**Controls on Fluvial Hg Concentrations.** Instantaneous FTHg concentrations correlated positively with DOC at all sites except Beaverton Creek, Oregon, and with streamflow at all sites (Figure 2). FMeHg patterns were more complicated; there does not appear to be a common response between FMeHg and DOC or streamflow. At the four sites with moderate wetland areas (Pike, Evergreen, Santa Fe, and Little Wekiva), FMeHg was positively correlated with DOC and streamflow, similar to relationships observed for FTHg. This pattern is expected, as high flows should flush MeHg from wetlands (11). Wet conditions accompanying high flows also increase the extent of inundation in wetland soils, thereby increasing the areal extent of soils with enhanced Hg methylation (12). In contrast, in the St. Marys River (Florida),



**FIGURE 2.** Filtered total mercury and methylmercury versus dissolved organic carbon (DOC) and streamflow. Regression lines are plotted if significant ( $p < 0.05$ ). The method detection limit (MDL) of  $0.04 \text{ ng L}^{-1}$  is plotted as a horizontal line; censored ( $< \text{MDL}$ ) data are plotted at  $0.02 \text{ ng L}^{-1}$ . No regression was performed for FMeHg at Lookout Creek, Oregon, due to low detection frequency.

a high-MeHg stream, FMeHg decreased with increasing streamflow and showed no significant relation to DOC. This river drains a large wetland (Okefenokee Swamp), which likely



**FIGURE 3.** Mean FTHg and FMeHg versus wetland abundance. The following equations describe the regression lines: Mean  $\text{FTHg} = 0.431 + 0.113W$ , and Mean  $\text{FMeHg} = -0.00441 + 0.00977W$ , where  $W$  = wetland abundance as a percentage of basin area (sum of herbaceous and woody wetlands; see ref 7). For FMeHg (which includes censored data), plotted values are geometric means calculated from the maximum likelihood estimate of mean  $\log[\text{FMeHg}]$ .

is an important zone of Hg methylation. Under high flow conditions, upland portions of the St. Marys River basin also contribute runoff and elevated concentrations of FTHg and DOC; however, FMeHg appears to be diluted when upland contributions are important.

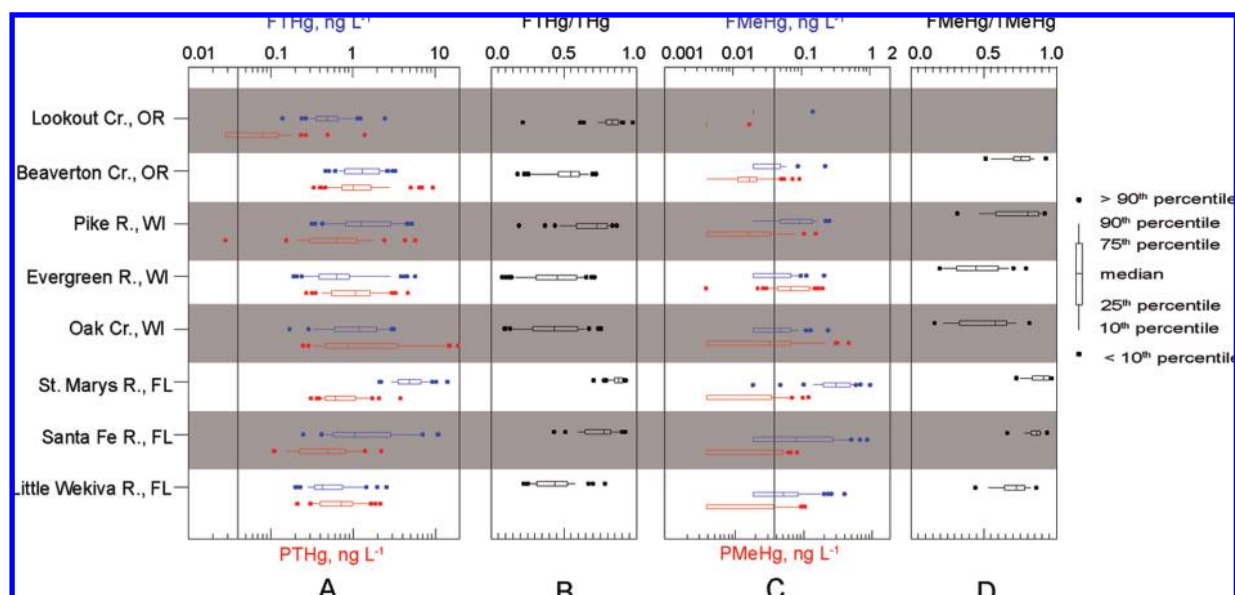
Although the negative FMeHg–streamflow relationship in the St. Marys River was anomalous compared to the other streams, reports of negative correlations are not unprecedented and emphasize the importance of local site conditions. Hammerschmidt et al. (13) report a negative MeHg–streamflow correlation for a small arctic stream with much lower MeHg concentrations than those reported for the St. Marys River. Bishop et al. (14) reported a dilution of MeHg in spring snowmelt runoff in forested catchments, and Balogh et al. (12) reported episodes of high MeHg in streams at low flows, particularly during autumn leaf-fall periods, with modest MeHg levels during summer high-flow events.

FMeHg concentrations were lower in streams with less wetland abundance. At Lookout Creek and Beaverton Creek, Oregon, no significant correlations to DOC or streamflow were observed, whereas at Oak Creek, Wisconsin, FMeHg concentrations were weakly correlated with DOC and uncorrelated with streamflow.

Mean FTHg and FMeHg concentrations for each stream were strongly correlated with wetland abundance (expressed as a percentage of the catchment; Figure 3). Although these correlations are strongly influenced by one stream basin with high wetland abundance, our findings, based on sampling across seasons and flow conditions in a wide variety of environmental settings, corroborate earlier reports of the importance of wetlands on the production of MeHg in the environment (4, 15).

Log-transformed concentrations of particulate forms of Hg also correlated with streamflow (not shown). Seven of eight sites had significant correlations between PTHg and flow ( $r^2 = 0.21$ – $0.69$  and  $p \leq 0.001$ ), the exception being Lookout Creek, Oregon. Six of eight sites had significant correlations between PMeHg and flow ( $r^2 = 0.19$ – $0.70$  and  $p < 0.003$ ), the exceptions being Lookout Creek, Oregon, and





**FIGURE 4.** Distributions of (A) filtered total mercury (FTHg) and particulate total mercury (PTHg), (B) FTHg/THg, (C) filtered methylmercury (FMeHg) and particulate methylmercury (PMeHg), and (D) FMeHg/TMeHg. For A and C, the vertical line at 0.04 ng L<sup>-1</sup> is the method detection limit (MDL) for FTHg and FMeHg; censored (<MDL) values were set to half the lowest reported value (0.02 ng L<sup>-1</sup> for FTHg and FMeHg; variable for PTHg and PMeHg). For each site, upper (blue) and lower (red) boxplots are for filtered and particulate forms, respectively. For B and D, censored data were excluded from calculations.

St. Marys River, Florida. Lookout Creek typically carries low SS concentrations (median = 1 mg L<sup>-1</sup>). In contrast, St. Marys River carries moderate SS concentrations (median = 98 mg L<sup>-1</sup>), but SS is uncorrelated with streamflow at this site.

Although much of the emphasis of this paper is on Hg in filtered water, many researchers and monitoring agencies measure Hg in whole water (unfiltered) samples containing both dissolved and particulate forms of Hg. DOC concentrations account for much of the variability ( $r^2 = 0.63$ ) in THg<sub>ww</sub> (sum of FTHg and PTHg concentrations) among all eight sites (maximum likelihood regression of log-transformed data). Adding terms for streamflow and SS (eq 3) improved the regression slightly:

$$\log[\text{THg}_{\text{ww}}] = 0.1664 + 0.6079 \log[\text{DOC}] + 0.2358 \log[Q/\text{da}] + 0.1318 \log[\text{SS}] \quad (r^2 = 0.74) \quad (3)$$

where  $Q$  = streamflow (m<sup>3</sup> s<sup>-1</sup>) and  $\text{da}$  = drainage basin area (km<sup>2</sup>). DOC and SS can be thought of as carriers of Hg (16, 17), and although both are typically positively correlated with streamflow, the addition of a streamflow term may account for the changing character of DOC and SS as a function of streamflow. A similar equation was derived for calculated MeHg<sub>ww</sub> (sum of FMeHg and PMeHg; eq 4):

$$\log[\text{MeHg}_{\text{ww}}] = -1.935 + 0.8435 \log[\text{DOC}] + 0.0924 \log[Q/\text{da}] + 0.1945 \log[\text{SS}] \quad (r^2 = 0.48) \quad (4)$$

Although log-transformed concentrations of DOC and SS correlate positively ( $r = 0.66$ ), DOC appeared to be more important than SS in describing THg<sub>ww</sub> concentrations. This may be the result of selecting streams that carry low to moderate levels of SS but that have a wide range in DOC concentrations. In contrast, Balogh et al. (18) report a dominant influence of total suspended solids in agricultural Minnesota streams with considerably higher suspended solids concentrations than our study streams. The relative abundance of particulate versus filtered forms of both THg and MeHg varied greatly within and among our study streams, depending on the availability of DOC and SS (Figure 4). This is consistent with previous studies (16). Further, Grigal (16) noted similarities among THg–DOC relationships in studies

of lakes and streams across the northern U.S. Models of Hg transport in streams, therefore, should account for both DOC-bound and SS-bound Hg. Refinements might be made by relating particulate Hg to measured sediment characteristics, such as particulate organic carbon (17), particle size, and mineral composition, and to differences in the composition and reactivity of DOC.

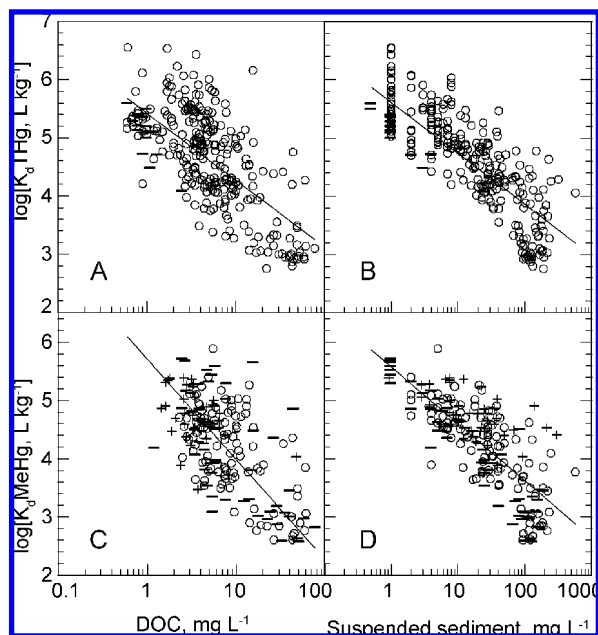
**Filtered-Particulate Distributions.** The distribution of Hg between filtered and particulate forms varied greatly, both within and among sites (Figure 4). The fraction of filtered Hg ranged from about 0.075 to 0.97 for FTHg/THg and from 0.17 to 0.97 for FMeHg/TMeHg. The fraction of filtered Hg tended to be higher at low-SS, nonurban sites, whereas particulate Hg dominated at the urban sites and Evergreen River, Wisconsin, which typically had higher SS concentrations.

Distribution coefficients ( $K_d$ ) for THg in the water column were calculated as

$$K_d = \frac{[\text{PTHg}]/[\text{SS}]}{[\text{FTHg}]} \quad (5)$$

where PTHg and FTHg are in nanograms per liter and SS is in kilograms per liter, resulting in  $K_d$  units of liters per kilogram.  $K_d$  values for MeHg were calculated similarly. Log-transformed distribution coefficients ( $\log[K_d]$ ) for THg ranged from 2.8 to 6.6 (median = 4.8); for MeHg, values ranged from 2.6 to 5.9 (median = 4.4, based on uncensored data; Figure 5). Others have reported similar ranges in  $\log[K_d]$  among a diverse set of streams for both THg [ $\sim 2.8$ – $6.1$  (15),  $2.8$ – $5.5$  (19)] and MeHg [ $2.9$ – $5.8$  (19)].  $K_d$  for both THg and MeHg showed similar distributions (Figure 5), except the distribution for MeHg was truncated due to samples that had censored concentrations for both FMeHg and PMeHg.

$K_d$  for both THg and MeHg decreased with increasing DOC, indicating a decreasing relative fraction of particulate-associated Hg in streamwater containing greater amounts of DOC. A similar trend in  $K_d$  versus DOC has been reported for particulate material in lakes (20). The published literature generally holds that only the dissolved Hg fraction is available for methylation, an assertion that, if correct, is supported by this study, which generally shows a good correspondence between low  $K_d$  (high DOC) and elevated levels of MeHg in



**FIGURE 5.** Log-transformed distribution coefficients ( $K_d$ ) of THg and MeHg versus DOC and suspended sediment concentrations. Symbols denote detection of particulate and filtered forms of Hg (○), left-censored  $K_d$  (particulate Hg < MDL) (—), and right-censored  $K_d$  (filtered Hg < MDL) (+). If both filtered and particulate forms of Hg were <MDL,  $K_d$  was not calculated. Maximum likelihood regression equations: (A)  $\log[K_d\text{THg}] = 5.42 - 1.15 \log[\text{DOC}]$ ,  $r^2 = 0.41$ ; (B)  $\log[K_d\text{THg}] = 5.61 - 0.875 \log[\text{SS}]$ ,  $r^2 = 0.61$ ; (C)  $\log[K_d\text{MeHg}] = 5.71 - 1.72 \log[\text{DOC}]$ ,  $r^2 = 0.39$ ; (D)  $\log[K_d\text{MeHg}] = 5.58 - 0.976 \log[\text{SS}]$ ,  $r^2 = 0.29$ .

streamwater. In the absence of a true marker of bioavailability, however, these relations can only be inferred.

$K_d$  also decreased with increasing SS, a trend consistent with observations from other streams (19, 21). Decreasing  $K_d$  values with increasing solids concentrations have been observed for other hydrophobic compounds, including heavy metals, both in laboratory experiments and in natural waters (22, 23). This relationship has been attributed to increasing amounts of filter-passing colloidally bound constituents with increasing concentrations of particulates (23).

In streams, DOC and SS typically co-vary with streamflow. Furthermore, DOC and SS likely differ in character under different streamflow regimes (chemical reactivity for DOC; particle-size distribution and organic content for SS). SUVA increased with increasing streamflow at six of eight of our sites (not shown, data in ref 8), indicating a tendency toward export of more highly aromatic DOC of terrigenous origin at higher flows (24). We did not measure particulate organic carbon content; however, others have reported increasing PTHg with increasing organic content of SS in tributaries to Lake Champlain (25). Variation in DOC and SS concentration and character may influence both the slope and noise in the  $K_d$ –SS relationship. Mechanistic models of Hg cycling that use  $K_d$ , SS, and DOC as model parameters should, therefore, account for variations of these parameters.

**Atmospheric Inputs and Fluvial Export.** All ecosystem Hg inputs were assumed to result from atmospheric deposition (2). Annual wet THg deposition varied by a factor of ~4 among sites (Table 1) and effectively captured most of the range in THg deposition across the continental U.S., as measured by the National Atmospheric Deposition Program's Mercury Deposition Network (MDN) (<http://nadp.sws.uiuc.edu/mdn/>). Wet deposition of MeHg, a small component of THg in precipitation (26), varied by a factor of ~5 across the sites and decreased from the northwestern to southeastern sites. The percentage of THg as MeHg in wet deposition also

decreased along the same spatial gradient: Oregon (4.6–4.9%), Wisconsin (0.9–2.0%), and Florida (0.3–0.6%).

Annual fluvial THg export, as a percentage of annual atmospheric input, was highly variable among stream basins, but less than 50% in all cases (Table 1). Impervious surfaces have the potential to short-circuit hydrologic pathways in stream basins and thus reduce retention (increase yield) of atmospherically derived Hg (21, 27). THg export was greatest in the Oregon urban stream (24–44%), which drains the basin with the greatest density of impervious surfaces (Table 1). However, THg export was comparatively low (3–22%) in the other two urban streams (Wisconsin and Florida); these latter two basins had substantial impervious cover, although somewhat lower than the Oregon urban basin.

Fluvial export of TMeHg, as a percentage of atmospheric input, varied greatly among streams, ranging from 3% to values exceeding 100%, suggesting substantial production of MeHg in the basin and delivery to the stream (Table 1). Florida sites tended to have the highest percentages of atmospheric MeHg load delivered as fluvial load, resulting from the large areal extent of wetlands in the two nonurban basins. The input–output comparison has limitations in a mass-balance context due to the complexities of MeHg cycling in natural ecosystems (MeHg production via methylation of  $\text{Hg}^{\text{II}}$  and MeHg loss via demethylation and storage), and because yields of constituents from stream basins tend to decrease with increasing basin size (e.g., ref 28).

Additional inferences can be made regarding which ecosystem compartments account for most of the MeHg observed in streams, particularly for ecosystems that receive Hg predominantly via atmospheric deposition. First, the positive correlation between FMeHg and streamflow at three sites where FMeHg was frequently detected (Pike, Santa Fe, Little Wekiva Rivers; Figure 2) suggests that runoff from these basins is the dominant contributor of MeHg. If benthic production of MeHg within the stream channel were the more important process, one would expect a negative correlation between FMeHg and streamflow, reflecting a dilution of channel-produced MeHg at high flows. The anomalous behavior of FMeHg at the St. Marys River, Florida, site can be explained by the differences in local water sources in this basin at low versus high flows, as discussed previously. Second, all relevant measures of MeHg in streambed sediment (sediment MeHg concentration, porewater MeHg concentration, and experimental methylation rate measurements (5)) lacked positive correlation to MeHg concentrations in the water column. Third, the relationship observed between FMeHg and wetland density supports the notion that wetlands are a dominant ecosystem compartment responsible for MeHg production and export to adjoining aquatic ecosystems (4, 15). We conclude that benthic, in-channel production of MeHg is not important to the mass balance of MeHg within the studied stream basins, whereas MeHg production in hydrologically connected wetlands and delivery to the streams via runoff is likely the predominant source of MeHg to streams.

Although atmospheric Hg deposition and the concentrations of most forms of fluvial Hg tended to increase from Oregon to Wisconsin to Florida, variations in Hg deposition appear less important than basin characteristics in governing fluvial THg and MeHg concentrations. The sites chosen for this study span an approximate 3-fold range in annual wet depositional fluxes of THg, and a 3- to 4-fold range in spatially averaged estimates of THg flux (Table 1). No correlations were observed between atmospheric inputs and fluvial concentrations or loads of THg. Within a given region, considerable variation in fluvial THg and MeHg was observed. For example, in Florida, Hg deposition among the three sites varied by a factor of 1.30–1.32 (THg low and high estimates,

Table 1), whereas median fluvial THg<sub>ww</sub> concentration (sum of median FTHg and PTHg, Supporting Information Table S4) varied by a factor of 4.78. A useful conceptual model is that the quantity of Hg entering an ecosystem sets the baseline Hg concentrations for a region, whereas ecosystem properties govern the range of how much Hg and MeHg enters streams within a region. Changes in source or ecosystem properties will likely influence fluvial Hg concentrations and speciation. In addition to loading and basin properties, short-term (antecedent moisture, rainfall intensity, temperature) and long-term (trends in frequency of large events, temperature trends) climatic factors also likely play important roles in governing fluvial Hg concentrations, speciation, and loads. Better understanding of temporal dynamics associated with deposition and fluvial Hg is needed to improve prediction of ecosystem responses.

Our observations suggest two simple screening tools for geographically broad predictions of fluvial Hg transport for areas receiving Hg predominantly from atmospheric deposition. First, evaluation of existing DOC, SS, and streamflow data could be used to identify streams likely to have high Hg concentrations. Second, wetland abundance in a river basin is strongly linked to dissolved Hg species, especially MeHg. These simple tools could provide useful insights into Hg in stream ecosystems, by identifying areas for more focused assessment.

## Acknowledgments

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## Supporting Information Available

A description of atmospheric mercury deposition estimates and additional supporting data tables are presented. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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